

Universality in the transport response of molecular wires physisorbed onto graphene electrodes

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(Dated: March 7, 2013)

We analyse the transport response of large molecular wires bridging graphene electrodes, where the molecules are physisorbed onto the graphene sheets. In our study, the sheets are pulled away to vary the gap length and the relative atomic positions. The molecular wires are also translated in directions parallel and perpendicular to the sheets. We show that the energy position of the molecular resonances is universal for a given molecule, in the sense that it is independent of the details of the graphene edges, gaps lengths or of the molecule positions. Although the junctions discussed here show a large variability in the zero-bias conductance, we suggest that this variability can be reduced drastically by suitably tuning the energy position of the HOMO or LUMO resonances to low enough energies.

PACS numbers: 72.80.Vp, 85.65.+h, 73.63.Rt, 71.15.Mb

Single- or few-molecule electronics was considered for some time a plausible alternative technology to silicon, that could be deployed to enable reaching the atomic limit^{1,2}. However, the picture that has emerged along the past few years is that single-molecule junctions show a serious lack of mechanical robustness together with a large variability in the electrical response. These drawbacks are linked directly or indirectly to the few-particle nature of the contacts in these devices. For example, the lack of conductance reproducibility arises from the large phase space of coupling configurations with different conductances. Hence, it is impossible to attach a precise value of conductance for a given combination coupling group/metal. Instead, experimental results are presented in terms of statistically averaged conductance histograms³. The lack of reproducibility is being reduced by the use of a new generation of contact groups⁴⁻⁶, but this improvement is marginal.

Graphene electrodes could be used as an alternative to conventional metallic electrodes to help solving this lack of reproducibility. The use of this material brings about several clear advantages. First, the lack of atomic diffusivity in graphene makes each gap geometry stable over time. Second, graphene's planar nature enables the visualization of the junctions, and possibly the control over the actual molecule positioning. Third, graphene allows more easily for gateable junctions. A number of theoretical articles have indeed proposed bridging graphene electrodes with molecules, whose anchor groups would be chemisorbed to the electrodes' edges⁷⁻¹¹. An alternative approach was advanced in Refs. (12,13), where fullerene-based dumbbell wires were physisorbed onto graphene, or molecular wires were physisorbed onto carbon nanotubes. By contacting the molecules deep inside the sheets, trouble related to the size-mismatch between the physical gap and the length of the molecule is avoided from the outset¹². In addition, the conductance variability inherent to the tribological nature of graphene's edges is avoided¹⁰. Recently it was also proven experimentally that stable and gateable molecular junctions can be formed by depositing molecules on top of a graphene nanogap fabricated by electroburning¹⁴, where the molecules'

anchor groups were probably contacting the edges.

In this manuscript we explore the electronic properties and the electrical response of molecular wires physisorbed onto graphene leads. Physisorption is a gentler attachment to graphene than chemisorption. The distortion of the geometry and the electronic structure of both molecule and graphene's contact area is expected to be only moderate and mostly related to screening effects. Specifically, charge transfer between molecule and electrodes is strongly suppressed so the contact-induced dipoles are expected to be small. In contrast to Ref. (12), we analyze molecular wires with planar anchor groups such as porphyrine or phthalocyanine molecules. These groups are linked by polyine chains to form dimer and trimer wires, an example of which is shown in Fig. (1). The rationale behind our choice is that increasing the contact surface area could enhance the mechanical stability of the junctions and provide an effective conductance averaging. In addition, porphyrine wires show a small conductance decay with wire length when contacted by gold electrodes¹⁵. Porphyrine wires can also show interference and spin-filtering effects that make them promising functional units¹⁶. As opposed to dumbbell molecules, the central region in our wires is by geometrical constraints placed always at the same height measured from the graphene layers, bringing a desirable degree of isolation to the functional central unit and, therefore, of reproducibility.

Our main result is a remarkable universality in the energy position of the molecular levels, which is completely missing for junctions comprising noble-metal electrodes, or for edge-contacted graphene junctions. Specifically, we find that the energy position of the molecular levels does not shift when the molecules are displaced, or when the graphene sheets are pulled away to vary the physical gap length. These universality property suggests that the conductance variability can be reduced by appropriate tuning of the energy position of the lowest-lying molecular levels.

We will discuss our results in terms of the junction shown in Fig. (1), where a trimer molecule made up of three porphyrin units is linked by butadiynes, e.g.: atomic chains made of four carbon atoms. We expect that this molecule will be placed

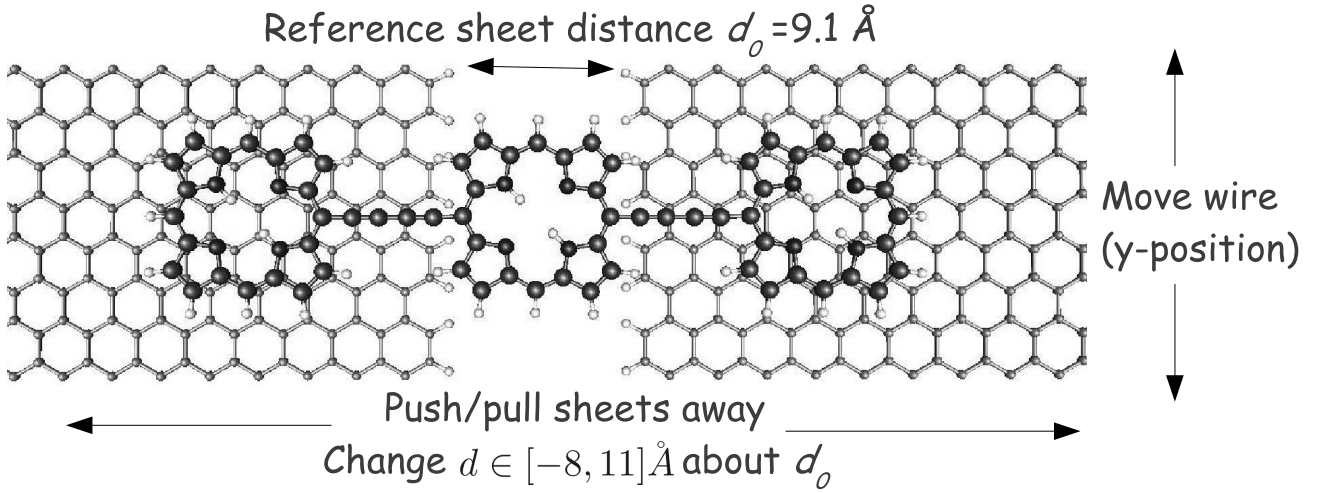


FIG. 1: (Color online) Extended molecule used to calculate the transport properties. Small light-grey (graphene) and large dark-grey (molecule) spheres and small white spheres represent carbon and hydrogen atoms, respectively. Medium-size spheres around the center of each porphyrin ring represent nitrogen atoms. The system has a total of 446 atoms.

roughly at the same height above the sheets ($\sim 3.2 \text{ \AA}$), regardless of its position. Hence, we will discuss the changes in the transmission coefficients and in the conductance when the molecule is displaced across the plane in directions parallel and perpendicular to the edges, or when the graphene sheets are pulled away or pushed towards each other. The sheets shown in Fig. (1) are terminated in a zigzag configuration, and passivated by hydrogen atoms in a 1-1-1-sequence. However we expect that edges will have a reduced impact when the anchors attach deep inside the sheets. We used the Density Functional Theory code SIESTA¹⁷, which employs norm-conserving pseudopotentials to account for the core electrons and linear combinations of atomic orbitals to construct the valence states. In order to better describe physisorption, we used a recent implementation¹⁸ of the van der Waals functional of Dion et al¹⁹. We computed the Hamiltonian and overlap matrix elements, the potential and the density using a real-space grid with fineness defined with an equivalent energy cutoff of 200 Ry. We relaxed quickly the coordinates to forces smaller than 0.05 eV/\AA using a single- ζ basis set (SZ). We took then these coordinates as seeds for further coordinate relaxation using a single- ζ polarized (SZP). We repeated the procedure now with a double- ζ (DZ) and then with a double- ζ polarized (DZP). We first relaxed an isolated porphyrin ring on top of graphene and used those coordinates as a starting point to construct the junction by joining the carbon chains and the central porphyrin ring. Tests performed with one of the junctions showed that there are not very large differences in the positions calculated with different basis sets. The electronic structure is however very sensitive to the choice of the basis: we found large differences in the transmission and the density of states when the basis set improved from SZ to SZP and to DZ. There were not however many changes in moving from DZ to DZP, which implies that the electronic structure is well converged with DZ. We used then this basis set to perform all calculations. The junctions analyzed here were

made periodic along the direction perpendicular (y) to electronic transport (z). We kept only the gamma point in our calculations because the lateral size of the graphene electrodes is large enough to have reduced finite-size effects. Each electrode has 10 principal layers, where each principal layer has two columns of carbon atoms. This was enough to accommodate the porphyrin molecules on top of the sheets and ensure that the electronic structure converges to the bulk electronic structure at the leftmost and rightmost layers. The graphene layers were pulled/pushed along the z -axis opposite to each other, so that the physical gap length d increased or decreased. We chose a reference distance d_0 between layers equal to 9.1 \AA . This corresponded to the separation in which the central porphyrin covers entirely the gap. We varied the gap between $d = -7.6 \text{ \AA}$ and $d = 11.2 \text{ \AA}$ in steps of 0.2 \AA .

The transport properties were computed using the multi-scale transport code GOLLUM²⁰. The zero-voltage transmission coefficients $T(E, V = 0)$ as the electrodes gap length changes from d_0 are plotted in Fig. (2), at intervals of 0.8 \AA . The figure shows that the position of the molecular resonances remains almost constant. We have found that this behavior is universal. We have observed it for the present junction and also for a monomer, dimer or trimer made up of porphyrine or phthalocyanine planar groups physisorbed onto graphene. According to these results it is therefore possible to attach definite values of the molecular levels energy position to a given molecular wire. This universality could have been anticipated in fact: physisorption here carries no charge transfer between the molecule and the sheets, nor associated dipole moments. This is so because both sides of each contact are mostly made up of the same chemical species: carbon. Also, the $\pi - \pi$ hybridization between molecular orbitals and the electrode states is weaker than for the bonds present in most noble-metal/single-atom contacts, and does not have a large impact on the nature of the molecule orbitals. We note that this kind of universality should also be robust when strong

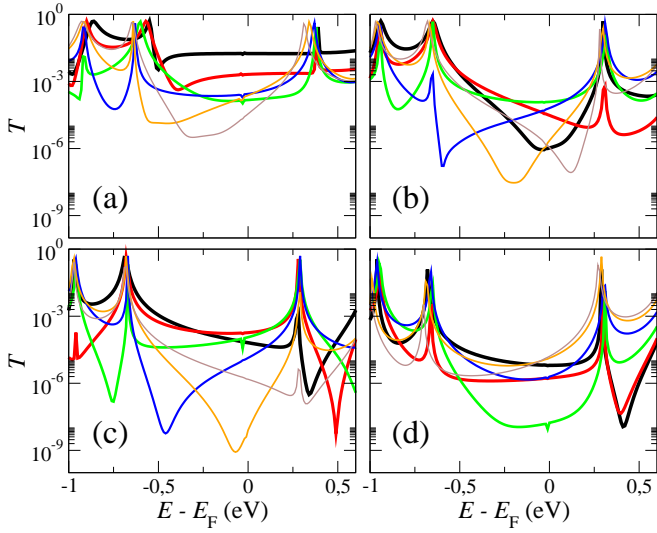


FIG. 2: (Color online) Evolution of the transmission $T(E)$ as the separation between the graphene layers d increases from -7.6 \AA to $+10.8 \text{ \AA}$ relative to d_0 , in steps of 0.8 \AA . Panels (a), (b) (c) and (d) correspond to curves in the intervals $[-7.6 \text{ \AA}, -3.6 \text{ \AA}]$, $[-2.8 \text{ \AA}, 1.2 \text{ \AA}]$, $[2.0 \text{ \AA}, 6.0 \text{ \AA}]$ and $[6.8 \text{ \AA}, 10.8 \text{ \AA}]$, respectively. Decreasing width of the lines corresponds to increasing d .

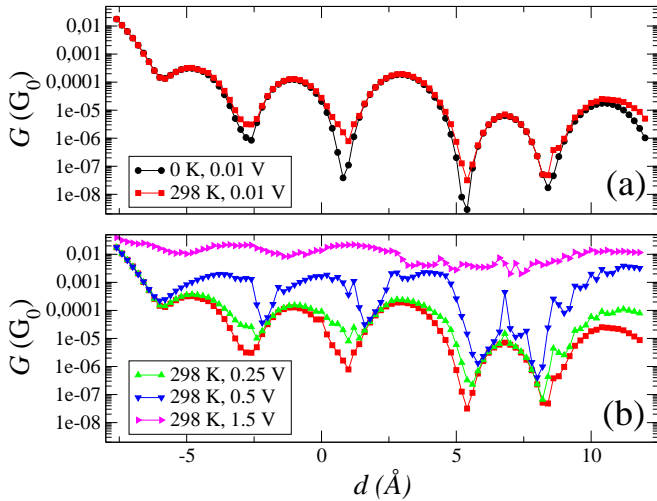


FIG. 3: (Color online) Evolution of the zero-bias conductance as the separation between the graphene layers along the transport direction (z) increases from -7.6 \AA to 11.2 \AA , relative to d_0 , for various voltages and temperatures.

correlations are included. Strong correlations must lead to a rearrangement of the electronic spectrum as compared to the DFT spectrum. Molecular resonances are shifted in energy and in some cases spitted into Lower/Upper Hubbard bands and/or a Kondo peak. However, even the strongly correlated spectrum should have these features always placed at the same energy position regardless of the relative disposition between molecular wire and graphene.

Fig. (2) also shows that $T(E)$ changes by orders of magnitude at energies E placed between two given molecular res-

onances, and in particular at the HOMO/LUMO gap. As a consequence, the low-voltage, low-temperature conductance $G = G_0 T(E_F, V = 0)$ shows strong variability as a function of the relative molecule/graphene position. An example is shown in the top panel of Fig. (3), where we plot G as a function of d . This panel also shows the room temperature conductance, computed using the approximate expression

$$G \simeq \frac{e}{hV} \int dE T(E, V = 0) (f(E + eV/2) - f(E - eV/2)) \quad (1)$$

The use of the above formula can be rationalized by noting that the voltage drop must be strongly localized at the contacts because of the physisorbed bond and should not have a strong impact on the transmission coefficient. Notice that, according to Fig. (3), finite temperatures lead only to a small reduction in the variability of G . In contrast, a finite voltage may have a much stronger impact on G , provided the energy integration window includes the HOMO/LUMO resonance, whichever is closest to the Fermi energy. This resonance, whose energy position is universal, will determine the conductance. We plot in the lower panel of Fig. (3) G as a function of d for several voltages. In the present case, the conductance is controlled by the HOMO, which is placed at about 0.75 eV below the Fermi energy. As a consequence, for voltages of order 1.5 eV , the conductance variability is reduced drastically. A closer knowledge can be gained by plotting G in a decimal, instead of a logarithmic scale. The conductance then still varies by a factor of 4 if the anchor groups interact with graphene's edges. We show G for distances $d > d_0$ in Fig. (4). Notice that the conductance is essentially constant when $2.5 \text{ \AA} < d < 8 \text{ \AA}$, which corresponds to gap lengths such that none of the three porphyrine molecules overlap with the edges.

It is relevant to argue now that organic synthetic chemistry is now developed to the level where molecules can be fabricated with a tailored energy spectrum, where the position of the HOMO and LUMO levels can be chosen a priori. This could be done for molecules isolated in vacuum, solution, or possibly deposited onto graphite. Longer linker groups than those used in the present study may also be synthesized to avoid graphene's edges.

We mention finally that we have computed the binding energy, E_B , for chemical detachment. Typically, we find energy barriers of the order of 2 eV , in agreement with a previous analysis²¹. However, we find energy barriers between adjacent minima for phthalocyanine monomers sliding on top of a graphene sheet $E_B \sim 40 \text{ meV}$, which are also consistent with a previous calculation²². We can make a rough estimate of the molecule's drift length $r \sim \sqrt{4Dt}$ using an Arrhenius equation for the diffusion constant

$$D = D_0 e^{-E_B/k_B T} \quad (2)$$

where we take $D_0 \sim 10^{-4} \text{ cm}^2/\text{s}$. We find that the molecule will drift quickly away from the junction except for temperatures below $5 - 10 \text{ K}$. Notice however that we have not taken account of graphene edges, which should help pinning the molecule to the physical gap.

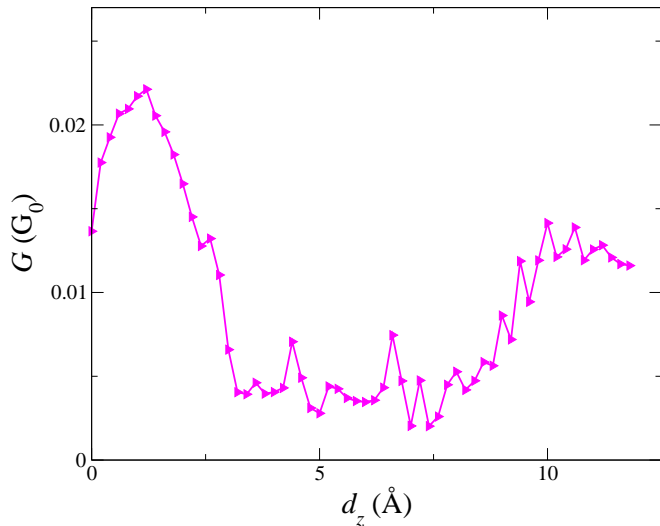


FIG. 4: (Color online) Evolution of the zero-bias conductance as the separation between the graphene layers along the transport direction (z) increases from 0.0 Å to 11.2 Å, relative to d_0 , for a voltage of 1.5 V and a temperature of 298 K.

In summary, we find that physisorbing molecular wires with large-area planar anchor groups onto graphene sheets shows universality properties whereby the molecular resonances are placed always at the same energy position regardless of the relative molecule/sheet position and of the phys-

ical gap length. This pinning is further enhanced if the anchor groups attach deep inside the sheets and do not overlap with graphene's edges. This universality property is a consequence of the iso-chemical nature of the physisorbed species. Our finding is sustained by DFT simulations of several graphene junctions bridged by monomeric, dimeric and trimeric molecular wires composed of porphyrine or phthalocyanine molecules. We have used a van der Waals functional that is suited for the problem at hand. We argue that even if the energy position of the molecular resonances is strongly rearranged by strong correlations, the new spectra should follow the same universality behavior. We suggest that the above property could be used to solve the conductance variability problem inherent to noble-metal-based single-molecule junctions. To do so, synthetic chemistry could be used to design molecules with HOMO or LUMO levels close enough to the Fermi energy that the low-voltage conductance is controlled by them. We finally find binding energies for molecule detachment of the order of 2 eV.

The research presented here was funded by the Spanish MICINN through the grants FIS2009-07081 and FIS2012-34858, and by the Marie Curie network NanoCTM. VMGS thanks the Spanish Ministerio de Ciencia e Innovación for a Ramón y Cajal fellowship (RYC-2010-06053). JF acknowledges useful discussions with M. Calame, M. Mayor, M. R. Bryce and C. J. Lambert. R. Ferrad s acknowledges conversations with J. J. de Miguel.

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